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ELEMENTS OF CHEMICAL REACTION ENGINEERING

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PRENTICE-HALL, Englewood Cliffs, New Jersey 07632

Library of Congress Cataloging-in-Publication Data

Fogler, H. Scott.
Elements of chemical reaction engineering.

(Prentice-Hall international series in the physical and chemical engineering sciences)
Includes bibliographies and index.
1. Chemical reactors. I. Title. II. Series.
TP157.F65 1986 660.2'81 85-28270
ISBN 0-13-263476-7

Manufacturing buyer: *Gordon Osbourne*

© 1986 by Prentice-Hall, Inc.
A Division of Simon & Schuster
Englewood Cliffs, New Jersey 07632

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Printed in the United States of America

10 9 8 7 6 5 4 3 2

ISBN 0-13-263476-7 025

Prentice-Hall International (UK) Limited, *London*
Prentice-Hall of Australia Pty. Limited, *Sydney*
Prentice-Hall Canada Inc., *Toronto*
Prentice-Hall Hispanoamericana, S.A., *Mexico*
Prentice-Hall of India Private Limited, *New Delhi*
Prentice-Hall of Japan, Inc., *Tokyo*
Prentice-Hall of Southeast Asia Pte. Ltd., *Singapore*
Editora Prentice-Hall do Brasil, Ltda., *Rio de Janeiro*
Whitehall Books Limited, *Wellington, New Zealand*

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1.4 Continuous-Flow Reactors

1.4.1 Continuous-stirred tank reactor

A type of reactor used very commonly in industrial processing is a stirred tank operated continuously (see Figure 1-4). It is referred to as the *continuous-stirred tank reactor* (CSTR) or *backmix reactor.* The CSTR is normally run at steady state, and is usually operated so as to be quite well mixed. As a result of the latter quality, the CSTR is generally modeled as having no spatial variations in concentration, temperature, or reaction rate throughout the vessel. Since the temperature and concentration are identical everywhere within the reaction vessel, they are the same at the exit point as they are elsewhere in the tank. Thus the temperature and concentration in the exit stream are modeled as being the same as those inside the reactor. In systems where mixing is highly nonideal, the well-mixed model is inadequate and we must resort to other modeling techniques, such as residence-time distributions, in order to obtain meaningful results. This topic is discussed in Chapters 13 and 14.

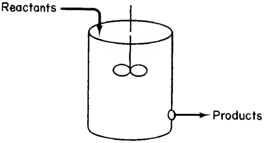

Figure 1-4 Continuous-stirred tank reactor.

When the general mole balance equation

$$F_{j0} - F_j + \int^V r_j \, dV = \frac{dN_j}{dt} \tag{1-4}$$

is applied to a CSTR operated at steady state (i.e., conditions do not change with time),

$$\frac{dN_j}{dt} = 0$$

in which there are no spatial variations in the rate of reaction, i.e.,

$$\int^V r_j \, dV = Vr_j$$

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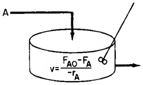
it takes the familiar form known as the *design equation* for a CSTR:



$$\boxed{V = \frac{F_{j0} - F_j}{-r_j}} \tag{1-6}$$

The CSTR design equation gives the reactor volume necessary to reduce the entering flow rate of species, j, F_{j0}, to the exit flow rate F_j. We note that the CSTR is modeled such that the conditions in the exit stream (e.g., concentration, temperature) are identical to those in the tank. The molar flow rate F_j is just the product of the concentration of species j and the volumetric flow rate v:

$$\boxed{\begin{array}{c} F_j = C_j \cdot v \\ \dfrac{\text{moles}}{\text{time}} = \dfrac{\text{moles}}{\text{volume}} \cdot \dfrac{\text{volume}}{\text{time}} \end{array}} \tag{1-7}$$

1.4.2 Tubular reactor

In addition to the batch and backmix (CSTR) reactors, another type of reactor commonly used in industry is the *tubular reactor.* It consists of a cylindrical pipe and is normally operated at steady state, as is the CSTR. For the purposes of the material presented here, we consider systems in which the flow is highly turbulent and the flow field may be modeled by that of plug flow. That is, there is no radial variation in concentration. (The laminar flow reactor is discussed in Chapter 13.)

In the tubular reactor, the reactants are continually consumed as they flow down the length of the reactor. In modeling the tubular reactor, we assume that the concentration varies continuously in the axial direction through the reactor. Consequently, the reaction rate, which is a function of concentration for all but zero-order reactions, will also vary axially. To develop the design equation, we shall divide (conceptually) the reactor into a number of subvolumes so that within each subvolume ΔV, the reaction rate may be considered spatially uniform (see Figure 1-5). We now focus our attention on the subvolume that is located a distance y from the entrance of the reactor. Letting $F_j(y)$ represent the molar flow rate of j into volume ΔV at y and $F_j\,(y + \Delta y)$ the molar flow of j out of the volume at the point $(y + \Delta y)$, the general mole balance on species j is

$$F_{j0} - F_j + \int^{V} r_j\, dV = \frac{dN_j}{dt} \tag{1-4}$$

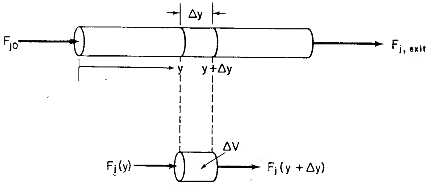


Figure 1-5 Tubular reactor.

In spatially uniform subvolume ΔV,

$$\int^{\Delta V} r_j\,dV = r_j\,\Delta V$$

For a tubular reactor operated at steady state,

$$\frac{dN_j}{dt} = 0$$

equation (1-4) becomes

$$F_j(y) - F_j(y + \Delta y) + r_j\,\Delta V = 0 \tag{1-8}$$

In this expression r_j is an indirect function of y. That is, r_j is a function of reactant concentration, which is a function of the position y down the reactor. The volume ΔV is the product of the cross-sectional area A of the reactor and the reactor length Δy.

$$\Delta V = A\,\Delta y$$

We now substitute in equation (1-8) for ΔV and then divide by Δy to obtain

$$-\left[\frac{F_j(y + \Delta y) - F_j(y)}{\Delta y}\right] = -Ar_j$$

The term in brackets resembles the definition of the derivative

$$\lim_{\Delta x \to 0}\left[\frac{f(x + \Delta x) - f(x)}{\Delta x}\right] = \frac{df}{dx}$$

Taking the limit as Δy goes to zero, we obtain

$$-\frac{dF_j}{dy} = -Ar_j$$

$\longrightarrow$ $F_{j,\,\text{exit}}$

(1-8)

ction of reactant
tor. The volume
e reactor length

Δy to obtain

or dividing by -1, we have

$$\frac{dF_j}{dy} = Ar_j \tag{1-9}$$

It is usually most convenient to have the reactor volume V rather than the reactor length y as the independent variable. Accordingly, we shall change variables using the relation $dV = A\,dy$ to obtain one form of the design equation for a tubular reactor:

$$\frac{dF_j}{dV} = r_j \tag{1-10}$$

We also note that for a reactor in which the cross-sectional area A varies along the length of the reactor, the design equation remains unchanged. This equation can be generalized for the reactor shown in Figure 1-6, in a manner similar to that presented above, by utilizing the volume coordinate V rather than a linear coordinate y. After passing through volume V, species j enters subvolume ΔV at V at a molar flow rate $F_j(V)$. Species j leaves subvolume ΔV at volume $(V + \Delta V)$ at a molar flow rate $F_j(V + \Delta V)$. As before, ΔV is chosen small enough so that there is no spatial variation of reaction rate within the subvolume:

$$G = \int^{\Delta V} r_j\, dV = r_j\,\Delta V \tag{1-11}$$

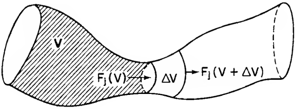


Figure 1-6

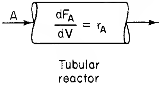
After accounting for steady-state operation in equation (1-4), it is combined with equation (1-11) to yield

$$F_j(V) - F_j(V + \Delta V) + r_j\,\Delta V = 0$$

Rearranging gives us

$$\frac{F_j(V + \Delta V) - F_j(V)}{\Delta V} = r_j$$

and taking the limit as $\Delta V \longrightarrow 0$, we again obtain equation (1-10):



$$\boxed{\frac{dF_j}{dV} = r_j} \tag{1-10}$$

Consequently, we see that equation (1-10) applies equally well to our model of tubular reactors of variable and constant cross-sectional area, although it is doubtful that one would find a reactor of the shape shown in Figure 1-6. The conclusion drawn from the application of the design equation is an important one: that the extent of reaction achieved in a plug-flow tubular reactor does not depend on its shape, only on its total volume.

To obtain some insight into things to come, consider the following example of how one can use the tubular reactor design equation (1-10).

Example 1-3 How Large Is It?

The first-order reaction

$$A \longrightarrow B$$

is carried out in a tubular reactor in which the volumetric flow rate is constant. Derive an equation relating the reactor volume to the entering and exiting concentrations of A, the rate constant k, and the volumetric flow rate v. Determine the reactor volume necessary to reduce the exiting concentration to 10% of the entering concentration when the volumetric flow rate is 10 dm^3/min (i.e., liters/min) and the specific reaction rate, k, is 0.23 per minute.

Solution

For a tubular reactor, the mole balance on species A ($j = \text{A}$) was shown to be

Reactor sizing

$$\frac{dF_A}{dV} = r_A \tag{1-10}$$

For a first-order reaction, the rate law (which is discussed in Chapter 3) is

$$-r_A = kC_A \tag{E1-3.1}$$

Since the volumetric flow rate, v_0, is constant,

$$\frac{dF_A}{dV} = \frac{d(C_A v_0)}{dV} = v_0 \frac{dC_A}{dV} = r_A \tag{E1-3.2}$$

Substituting for r_A in equation (E1-3.1) yields

$$-\frac{v_0\, dC_A}{dV} = -r_A = kC_A \tag{E1-3.3}$$

Rearranging gives us

$$-\frac{v_0}{k}\left(\frac{dC_A}{C_A}\right) = dV$$

Using the conditions at the entrance of the reactor that when $V = 0$, then $C_A = C_{A0}$,

$$-\frac{v_0}{k}\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^V dV \tag{E1-3.4}$$

This gives

$$V = \frac{v_0}{k} \ln \frac{C_{A0}}{C_A} \tag{E1-3.5}$$

Substituting C_{A0}, C_A, v_0, and k in equation (E1-3.5), we have

$$V = \frac{10\ \text{dm}^3/\text{min}}{0.23\ \text{min}^{-1}} \ln \frac{C_{A0}}{0.1 C_{A0}} = \frac{10}{0.23} \ln 10 = 100\ \text{dm}^3\ (100\ \text{liters};\ 0.1\ \text{m}^3)$$

We see that a reactor volume of 0.1 m^3 is necessary to convert 90% of species A entering into product B.

In the remainder of this chapter we look at slightly more detailed drawings of some typical industrial reactors and point out a few of the advantages and disadvantages of each.[†]

1.5 Industrial Reactors

When is a batch reactor used?

A batch reactor is used for small-scale operation, for testing new processes that have not been fully developed, for the manufacture of expensive products, and for processes that are difficult to convert to continuous operations.

The reactor can be charged (i.e., filled) through the two holes shown at the top (Figure 1-7). The batch reactor has the advantage of high conversions that can be obtained by leaving the reactant in the reactor for long periods of time, but it also has the disadvantages of high labor costs per unit production, and large-scale production is difficult.

Although a semibatch reactor (Figure 1-8) has essentially the same disadvantages as the batch reactor, it has the advantages of good temperature control and the capability of minimizing unwanted side reactions through the maintenance of a low concentration of one of the reactants. The semibatch reactor is also used for two-phase reactions in which a gas is usually continuously bubbled through the liquid.

What are the advantages and disadvantages of a CSTR?

A continuous-stirred tank reactor (CSTR) is used when intense agitation is required. The CSTR can either be used by itself or, in the manner shown in Figure 1-9, as part of a series or battery of CSTRs. It is relatively easy to maintain good temperature control with a CSTR. There is, however, the disadvantage that the conversion of reactant per volume of reactor is the smallest of the flow reactors. Consequently, very large reactors are necessary to obtain high conversions.

The tubular reactor [i.e., plug-flow reactor (PFR)] is relatively easy to maintain (no moving parts), and it usually produces the highest conversion per reactor volume of any of the flow reactors. The disadvantage of the tubular reactor is that it is difficult to control temperature within the reactor, and hot spots can

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[†] *Chem. Eng. 63* (10), 211 (1956). See also *AIChE Modular Instruction Series E*, Vol. 6 (to appear in 1986).

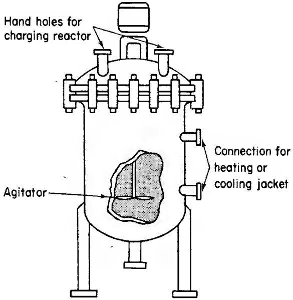
Hand holes for
charging reactor
Connection for
heating or
cooling jacket
Agitator

Figure 1-7 Simple batch homogeneous reactor. [Excerpted by special permission from *Chem. Eng.*, *63*(10), 211 (Oct. 1956). Copyright (1956) by McGraw-Hill, Inc., New York, NY 10020.]

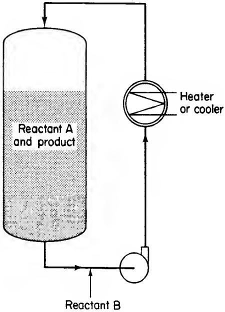
Reactant A
and product
Heater
or cooler
Reactant B

Figure 1-8 Semibatch reactor. [Excerpted by special permission from *Chem. Eng.*, *63*(10), 211 (Oct. 1956). Copyright (1956) by McGraw-Hill, Inc., New York, NY 10020.]

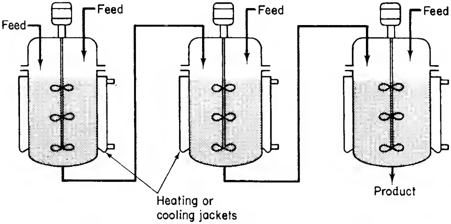

Figure 1-9 Battery of stirred tanks. [Excerpted by special permission from *Chem. Eng.*, *63*(10), 211 (Oct. 1956). Copyright (1956) by McGraw-Hill, Inc., New York, NY 10020.]

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What are the advantages and disadvantages of a PFR?

occur when the reaction is exothermic. The tubular reactor is commonly found either in the form of one long tube or as one of a number of shorter reactors arranged in a tube bank as shown in Figure 1-10. Most homogeneous liquid-phase

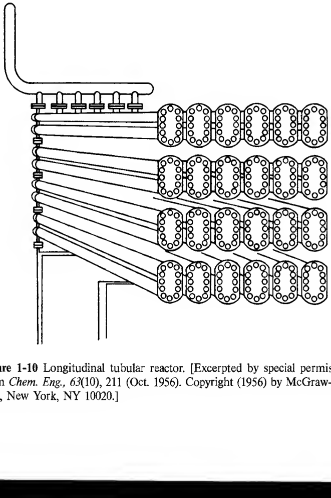

Figure 1-10 Longitudinal tubular reactor. [Excerpted by special permission from *Chem. Eng.*, *63*(10), 211 (Oct. 1956). Copyright (1956) by McGraw-Hill, Inc., New York, NY 10020.]

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flow reactors are CSTRs, whereas most homogeneous gas-phase flow reactors are tubular.

A fixed-bed (packed-bed) reactor is essentially a tubular reactor, which is packed with solid catalyst particles (Figure 1-11). This heterogeneous reaction system is used most frequently to catalyze gas reactions. This reactor has the same difficulties with temperature control as other tubular reactors, and in addition, the catalyst is usually troublesome to replace. On occasion, channeling of the gas flow occurs, resulting in ineffective use of parts of the reactor bed. The advantage of the fixed-bed reactor is that for most reactions it gives the highest conversion per weight of catalyst of any catalytic reactor.

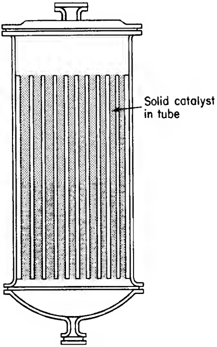

Figure 1-11 Longitudinal catalytic fixed-bed reactor. [Excerpted by special permission from *Chem. Eng.*, *63*(10), 211 (Oct. 1956). Copyright (1956) by McGraw-Hill, Inc., New York, NY 10020.]

Another type of catalytic reactor in common use is the fluidized-bed (Figure 1-12). The fluidized-bed reactor is analogous to the CSTR in that its contents, though heterogeneous, are well mixed, resulting in an even temperature distribution throughout the bed. The fluidized-bed reactor cannot be modeled as either a CSTR or a tubular reactor, but requires a model of its own. The temperature is relatively uniform throughout, thus avoiding hot spots. This type of reactor can handle large amounts of feed and solids, and has good temperature control; consequently, it is used in a large number of applications. The advantages of the ease of catalyst replacement or regeneration are sometimes offset by the high cost of the reactor and catalyst regeneration equipment.

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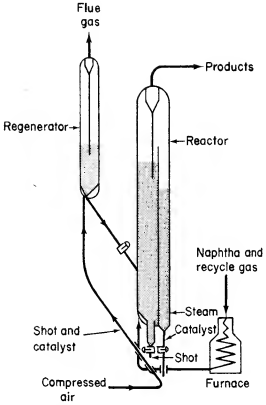
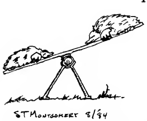

Flue gas
Products
Regenerator
Reactor
Naphtha and recycle gas
Steam
Catalyst
Shot and catalyst
Shot
Compressed air
Furnace

Figure 1-12 Fluidized-bed catalytic reactor. [Excerpted by special permission from *Chem. Eng., 63*(10), 211 (Oct. 1956). Copyright (1956) by McGraw-Hill, Inc., New York, NY 10020.]

The aim of the preceding discussion on commercial reactors is to give a more detailed picture of each of the major types of industrial reactors: batch, semibatch, CSTR, tubular, fixed-bed (packed-bed), and fluidized-bed. Many variations and modifications of these commercial reactors are in current use; for further elaboration, we refer the reader to the detailed discussion of industrial reactors given by Walas.[†]

SUMMARY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1. A **mole balance on species** *j*, which enters, leaves, reacts, and accumulates in a system volume *V*, is

$$F_{j0} - F_j + \int^{V} r_j \, dV = \frac{dN_j}{dt} \tag{S1-1}$$

[†] S. M. Walas, *Reaction Kinetics for Chemical Engineers* (New York: McGraw-Hill, 1959), Chap. 11.

2. The kinetic rate law for r_j is solely a function of the properties of the reacting materials; it is an intensive quantity. The rate law is essentially an algebraic equation of concentration, not a differential equation. For homogeneous systems, typical units of $-r_A$ may be gram moles per second per liter, and for heterogeneous systems, typical units of $-r'_A$ may be gram moles per second per gram of catalyst. By convention, $-r_A$ is the rate of disappearance of species A and r_A is the rate of formation of species A.
3. The **differential mole balance for a tubular reactor** operated at steady state is

$$\frac{dF_j}{dV} = r_j \tag{S1-2}$$

4. The **mole balance on a CSTR** (backmix reactor) can be expressed by the equation

$$V = \frac{F_{j0} - F_j}{-r_j} \tag{S1-3}$$

5. A **mole balance on a batch reactor** gives

$$\int^{V} r_j \, dV = \frac{dN_j}{dt} \tag{S1-4}$$

6. When there are no spatial variations in conditions and material properties within the reactor, equation (S1-4) can be written

$$\frac{1}{V}\frac{dN_j}{dt} = r_j \tag{S1-5}$$

QUESTIONS AND PROBLEMS

> I wish I had an answer for that, because I'm getting tired of answering that question.
>
> Yogi Berra, New York Yankees
> *Sports Illustrated*, June 11, 1984

P1-1 Make a list of the most important things that you learned in this chapter.

P1-2 What assumptions were made in the derivation of the design equation for
- **(a)** The batch reactor?
- **(b)** The CSTR?
- **(c)** The plug-flow reactor?

P1-3 State in words the meanings of $-r'_A$ and r'_A.

P1-4 Write the design equation for a backmix reactor that is not well mixed and consequently has a spatial variation in the reaction rate throughout the reactor volume.

Conversion and Reactor Sizing

2

Be more concerned with your character than with your reputation, because character is what you really are while reputation is merely what others think you are.

John Wooden, coach, UCLA Bruins

The first chapter focused on the general mole balance equation; the balance was applied to the three most common types of industrial reactors, and a design equation was developed for each reactor type. In Chapter 2 we first define *conversion* and then rewrite the design equations in terms of conversion. After carrying out this operation, we show how one may size a reactor (i.e., determine the reactor volume necessary to achieve a specified conversion) once the relationship between reaction rate, r_A, and conversion is known.

2.1 Definition of Conversion

In defining conversion, we choose one of the reactants as the basis of calculation and then relate the other species involved in the reaction to this basis. In most instances it is best to choose the limiting reactant as the basis of calculation. We develop the stoichiometric relationships and design equations by considering the general reaction

$$aA + bB \longrightarrow cC + dD \tag{2-1}$$

The capital letters represent chemical species and the lowercase letters represent stoichiometric coefficients. Taking species A as our basis of calculation, we divide

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the reaction expression through by the stoichiometric coefficient of species A, in order to arrange the reaction expression in the form

$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D \tag{2-2}$$

to put every quantity on a "per mole of A" basis.

A convenient way to relate the number of moles of each of the species in the reaction to one another is through the use of the quantity called **conversion.** The conversion X_A is the number of moles of A that have reacted per mole of A fed to the system:

Definition of X

$$X_A = \frac{\text{moles of A reacted}}{\text{moles of A fed}}$$

For the sake of brevity, we eliminate the subscript A and let $X \equiv X_A$. However, when considering multiple reactions (see Chapter 9) and certain other reaction schemes, it is often necessary to retain the subscript.

2.2 Design Equations

2.2.1 Batch systems

In most batch reactors, the longer the reactant is in the reactor, the more reactant is converted to product until either equilibrium is reached or the reactant is exhausted. Consequently, in batch systems the conversion X will be a function of the time the reactants spend in the reactor. If N_{A0} is the number of moles of A initially, then the total number of moles of A that have reacted after a time t is $N_{A0}X$:

$$\begin{bmatrix}\text{moles of A}\\ \text{consumed}\end{bmatrix} = \begin{bmatrix}\text{moles of A}\\ \text{fed}\end{bmatrix} \cdot \begin{bmatrix}\dfrac{\text{moles of A reacted}}{\text{mole of A fed}}\end{bmatrix}$$

$$\begin{bmatrix}\text{moles of A}\\ \text{reacted}\\ \text{(consumed)}\end{bmatrix} = \quad [N_{A0}] \quad \cdot \quad [X]$$

Now, the number of moles of A that remain in the reactor after a time t, N_A, can be expressed in terms of N_{A0} and X:

$$\begin{bmatrix}\text{moles of A}\\ \text{in reactor}\\ \text{at time } t\end{bmatrix} = \begin{bmatrix}\text{moles of A}\\ \text{initially fed}\\ \text{to reactor at}\\ t = 0\end{bmatrix} - \begin{bmatrix}\text{moles of A that}\\ \text{have been con-}\\ \text{sumed by chemical}\\ \text{reaction}\end{bmatrix}$$

$$N_A \quad = \quad [N_{A0}] \quad - \quad [N_{A0}X]$$

The number of moles of A in the reactor after a conversion X has been achieved is

$$\boxed{N_A = N_{A0} - N_{A0}X = N_{A0}(1 - X)} \tag{2-3}$$

When there are no spatial variations in temperature or concentration, the mole balance on species A for a batch system reduces to the following equation:

$$\frac{dN_A}{dt} = r_A V \tag{2-4}$$

This equation is valid whether or not the reactor volume is constant. In the general reaction

$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D \tag{2-2}$$

reactant A is disappearing; therefore, we multiply both sides of equation (2-4) by -1 to obtain the mole balance for the batch reactor in the form

$$-\frac{dN_A}{dt} = (-r_A)V \tag{2-5}$$

The rate of disappearance of A, $-r_A$, in this reaction might be given by a rate law similar to equation (1-2), such as $-r_A = kC_AC_B$.

For batch reactors we are interested in determining how long we should leave the reactants in the reactor in order to achieve a certain conversion X. To learn this, we transform the mole balance, equation (2-4), in terms of conversion by differentiating equation (2-3),

$$N_A = N_{A0} - N_{A0}X \tag{2-3}$$

with respect to time, while remembering that N_{A0} is the number of moles of A initially present and is therefore a constant with respect to time.

$$\frac{dN_A}{dt} = 0 - N_{A0}\frac{dX}{dt}$$

Combining with equation (2-4) yields

$$-N_{A0}\frac{dX}{dt} = r_A V$$

The differential forms of the design equations appear often in reactor analysis and are particularly useful in the interpretation of reaction rate data. **For a batch reactor, the design equation in differential form is**

Batch reactor

$$\boxed{N_{A0}\frac{dX}{dt} = -r_A V} \tag{2-6}$$

Constant-volume batch reactors are found very frequently in industry. In particular, the laboratory bomb reactor for gas-phase reactions is widely used for obtaining reaction rate information on a small scale. Liquid-phase reactions in which the volume change during reaction is insignificant are frequently carried out in batch reactors when small-scale production is desired or operating difficulties rule out the use of continuous systems. For a *constant-volume batch reactor*, equation (2-5) can be arranged into the form

$$-\frac{1}{V}\frac{dN_A}{dt} = -\frac{d(N_A/V)}{dt} = -\frac{dC_A}{dt} = -r_A \tag{2-7}$$

For batch-reactor systems in which the volume varies while the reaction is proceeding, the volume may usually be expressed either as a function of time alone or of conversion alone, for either adiabatic or isothermal reactors. Consequently, the variables of the differential equation (2-6) can be separated in one of the following ways:

$$V\,dt = N_{A0}\frac{dX}{-r_A}$$

or

$$dt = N_{A0}\frac{dX}{-r_A V}$$

These equations are integrated with the limits that the reaction begins at time zero (i.e., $t = 0, X = 0$). When the volume is varied by some external source in a specific manner such as a piston compressing the reacting gas according to the equation ($V = V_1 + V_2 \sin \omega t$), the equation relating time and conversion one would use is

$$\int_0^t V\,dt = N_{A0}\int_0^X \frac{dX}{-r_A} \tag{2-8}$$

However, for the more common batch reactors in which volume is not a predetermined function of time, the time t necessary to achieve a conversion X is

Design
equation

$$\boxed{t = N_{A0}\int_0^{X(t)} \frac{dX}{-r_A V}} \tag{2-9}$$

Equation (2-6) is the differential form of the design equation, and equations (2-8) and (2-9) are the integral forms for a batch reactor. The differential form is generally used in the interpretation of laboratory rate data.

2.2.2 Flow systems

Normally, the conversion increases with the time the reactants spend in the reactor. For continuous-flow systems, this time usually increases with increasing reactor volume; consequently, the conversion X is a function of the reactor volume

V. If F_{A0} is the molar flow rate of species A fed to a system operated at steady state, the molar rate at which species A is reacting within the entire system will be $F_{A0}X$. The molar feed rate of A *to* the system *minus* the rate of reaction of A within the system will *equal* the molar flow rate of A leaving the system F_A. The preceding sentence can be written in the form of a mathematical statement in the following manner:

$$[F_{A0}]\cdot[X] = \frac{\text{moles of A fed}}{\text{time}} \cdot \frac{\text{moles of A reacted}}{\text{moles of A fed}}$$

$$F_{A0}\cdot X = \frac{\text{moles of A reacted}}{\text{time}}$$

$$\begin{bmatrix}\text{molar flow rate}\\ \text{at which A is}\\ \text{fed to the system}\end{bmatrix} - \begin{bmatrix}\text{molar rate at}\\ \text{which A is}\\ \text{consumed within}\\ \text{the system}\end{bmatrix} = \begin{bmatrix}\text{molar flow rate}\\ \text{at which A leaves}\\ \text{the system}\end{bmatrix}$$

$$F_{A0} \qquad - \qquad F_{A0}X \qquad = \qquad F_A$$

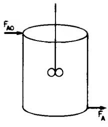
Rearranging gives us

$$\boxed{F_A = F_{A0}(1 - X)} \tag{2-10}$$

Using this relationship between molar flow rate and conversion, it is now possible to express the design equations in terms of conversion for the flow reactors examined in Chapter 1.

CSTR or Backmix Reactor The equation resulting from a mole (mass) balance on species A for the reaction

$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D \tag{2-2}$$



occurring in a CSTR was given by equation (1-6), which can be rearranged to

$$F_{A0} - F_A = -r_A V \tag{2-11}$$

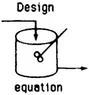
We now substitute for the exiting molar flow rate of A, F_A, in terms of the conversion X and the entering molar flow rate, F_{A0}, by using equation (2-10) in the form

$$F_{A0} - F_A = F_{A0}X$$

and combining it with equation (2-11) to give

$$F_{A0}X = -r_A V \tag{2-12}$$

We can rearrange equation (2-12) to determine the CSTR volume necessary to achieve a specified conversion X.



$$\boxed{V = \frac{F_{A0}X}{(-r_A)_{\text{exit}}}} \tag{2-13}$$

Since the exit composition from the reactor is identical to the composition inside the reactor, the rate of reaction is evaluated at the exit conditions.

Tubular Flow Reactor After multiplying both sides of the tubular reactor design equation (1-10) by -1, we express the mole balance equation for species A in the reaction given by equation (2-2) as

$$\frac{-dF_A}{dV} = -r_A \tag{2-14}$$

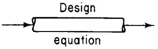
For a flow system, F_A has previously been given in terms of the entering molar flow rate F_{A0} and the conversion X:

$$F_A = F_{A0} - F_{A0}X \tag{2-10}$$

Combining equations (2-10) and (2-14), the result is the differential form of the design equation of a plug-flow reactor:

$$F_{A0}\frac{dX}{dV} = -r_A \tag{2-15}$$

We now separate the variables and integrate with the limit $V = 0$ when $X = 0$ to obtain the plug-flow reactor volume necessary to achieve a specified conversion X:



$$\boxed{V = F_{A0}\int_0^X \frac{dX}{-r_A}} \tag{2-16}$$

To carry out the integrations in the batch and plug-flow reactor design equations (2-9) and (2-16), as well as evaluation of the CSTR design equation (2-13), we need to know how the reaction rate $-r_A$ varies with the concentration (hence conversion) of the reacting species. This relationship between reaction rate and concentration is developed in Chapter 3.

2.3 Applications of the Design Equations

The rate of disappearance of A, $-r_A$, is almost always a function of the concentrations of the various species present. When a single reaction is occurring, each of the concentrations can be expressed as a function of the conversion X; consequently, $-r_A$ can be expressed as a function of X.

A particularly simple functional dependence, yet one that does occur on many occasions, is $-r_A = kC_{A0}(1 - X)$. For this dependence, a plot of the reciprocal rate of reaction $(-1/r_A)$ as a function of conversion yields a curve similar to the one shown in Figure 2-1, where

$$\frac{1}{-r_A} = \frac{1}{kC_{A0}} \cdot \frac{1}{1 - X}$$

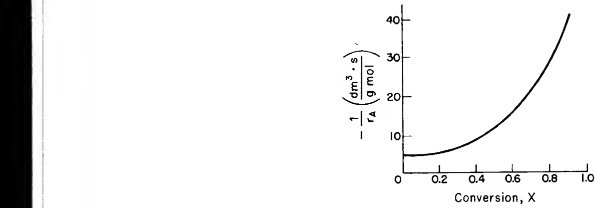


Figure 2-1

If a reaction is carried out isothermally, the rate is usually greatest when the concentration of reactant is greatest, i.e., when there is negligible conversion ($X \cong 0$). (Hence $1/-r_A$ will be small.) When the reactant concentration is small (i.e., when conversion is large), the reaction rate will be small. (Consequently, $1/-r_A$ is large.) For irreversible reactions of greater than zero order,

$$-\frac{1}{r_A} \longrightarrow \infty \quad \text{as} \quad X \longrightarrow 1$$

These characteristics are illustrated by Figure 2-1 and the majority of reactions exhibit qualitatively similar curves.

Example 2-1 Sizing a CSTR

Shade the area in Figure 2-1 which, when multiplied by F_{A0}, would give the volume of a CSTR necessary to achieve 80% conversion (i.e., $X = 0.8$).

Solution

Equation (2-13) gives the volume of a CSTR as a function of F_{A0}, X, and $-r_A$; i.e.,

$$V = \frac{F_{A0}X}{-r_A} \tag{2-13}$$

Algebraically,

$$V = F_{A0}\left(\frac{1}{-r_A}\right)X$$

$$\frac{V}{F_{A0}} = \left(\frac{1}{-r_A}\right)(0.8) \tag{E2-1.1}$$

In a CSTR the composition, temperature, and conversion of the effluent stream are identical to that of the fluid within the reactor since perfect mixing is assumed. Therefore, we need to find the value of $-r_A$ (or reciprocal thereof) when $X = 0.8$.

From Figure E2-1.1 we see that when $X = 0.8$, $1/-r_A = 27.5$.

$$\frac{V}{F_{A0}} = (27.5)(0.8) = 22 \text{ dm}^3\cdot\text{s/mol} \tag{E2-1.2}$$

It's the *rectangular* area for a CSTR

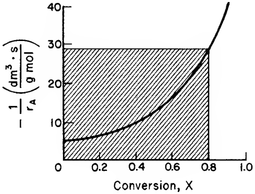


Figure E2-1.1

In Figure E2-1.1 this value of V/F_{A0} is equal to the area of a rectangle with a height $1/-r_A = 27.5$ and a base $X = 0.8$. This rectangle is shaded in the figure. If the entering molar flow rate, F_{A0}, was 20 mol/s, the CSTR reactor volume necessary to achieve 80% conversion would be

$$V = 20\,\frac{\text{mol}}{\text{s}} \cdot 22\,\frac{\text{dm}^3\cdot\text{s}}{\text{mol}}$$

$$= 440 \text{ dm}^3 = 440 \text{ liters}$$

The design equation for a plug-flow reactor (PFR) is

Design equation

$$V = F_{A0}\int_0^X \frac{dX}{-r_A} \tag{2-16}$$

It's the area *under* the curve for a plug-flow reactor

The integral in equation (2-16) can be evaluated from the area under the curve of a plot of $1/-r_A$ versus X (Figure 2-2). The product of this area and F_{A0} will give the tubular reactor volume necessary to achieve the specified conversion of A, X. For

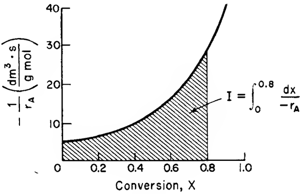


Figure 2-2

80% conversion the shaded area is roughly equal to 10 $dm^3 \cdot s/g$ mol. The tubular reactor volume can be determined by multiplying this area (in $dm^3 \cdot s/g$ mol) by F_{A0} (g mol/s). Shortcuts for evaluating the area under the curve in graphical integration are given in Appendix A.1.

Example 2-2 Comparing the CSTR and PFR Sizes

It is interesting to compare the volumes of a CSTR and a plug-flow reactor (PFR) required for the same job. To do this we shall use the data in Figure 2-1 to learn which reactor would require the smaller volume to achieve a conversion of 60%: a CSTR or a tubular reactor. The feed conditions are the same in both cases.

For the CSTR:

$$\frac{V}{F_{A0}} = \left(\frac{1}{-r_A}\right) X = (16)(0.6) = 9.6\ \frac{dm^3 \cdot s}{mol}$$

This is also the area of the rectangle with vertices $(X, 1/-r_A)$ of $(0, 0)$, $(0, 16)$, $(0.6, 16)$, and $(0.6, 0)$ (see Figure E2-2.1).

For the plug-flow (tubular) reactor:

$$\frac{V}{F_{A0}} = \int_0^{0.6} \frac{dX}{-r_A} = \text{area under the curve between } X = 0 \text{ and } X = 0.6$$

(see appropriate shaded area in Figure E2-2.1)

$$= 5.1\ \frac{dm^3 \cdot s}{mol}$$

For the same flow rate F_{A0}, the plug-flow reactor requires a smaller volume than the CSTR to achieve a conversion of 60%.

ol. The tubular
s/g mol) by F_{A0}
aphical integra-

-flow reactor
Figure 2-1 to
conversion of
same in both

0, 0), (0, 16),

$X = 0.6$
-2.1)

volume than

Generally, the isothermal tubular reactor volume is *smaller* than the CSTR for the same conversion

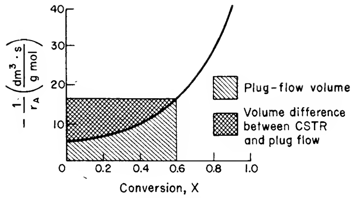


Figure E2-2.1

2.4 Reactors in Series

Many times reactors are connected in series such that the exit stream of one reactor is the feedstream for another reactor. When this occurs it is often possible to speed the calculations by defining the conversion in terms of location at a point downstream rather than with respect to any one reactor. That is, the conversion X is the total moles of A that have reacted up to that point per mole of A fed to the first reactor. However, this definition can only be used provided that there are no side streams withdrawn and the feedstream enters only the first reactor in the series.

As an example, the relationships between conversion and molar flow rates for the reactor sequence shown in Figure 2-3 are given by the following equations:

$$F_{A1} = F_{A0} - F_{A0}X_1$$

$$F_{A2} = F_{A0} - F_{A0}X_2$$

$$F_{A3} = F_{A0} - F_{A0}X_3$$

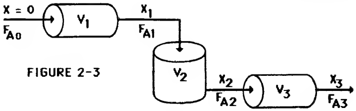


FIGURE 2-3

Figure 2-3